Ruthenium Oxide Glaze Resistors

NEW SCREEN PRINTING PREPARATIONS FOR THICK FILM CIRCUITRY

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The rapid development of thick film integrated circuits has created a need for preparations that will provide resistor films on a variety of substrates. In the development of the new range of materials described in this article advantage has been taken of the complex mechanism of conduction through ruthenium dioxide.

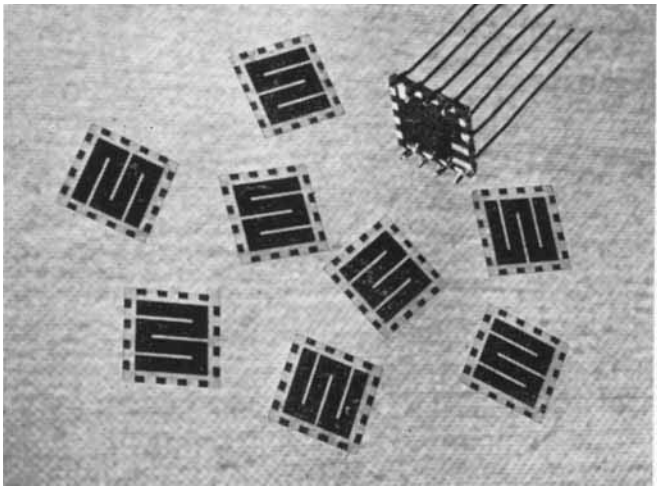
The past few years have witnessed mounting interest in integrated circuits and there is now little doubt that within the next decade a substantial proportion of electronic equipment will be based on them.

Conventional circuits are normally assembled from discrete components by soldering them on to a printed circuit board. In integrated circuits, on the other hand, the circuit elements are deposited as films on to substrates, a number of which are often assembled together. It was first believed that vacuum deposition was the ideal technique for producing these circuits, but within the past year silicon integrated circuits and, to a lesser extent, thick film circuits, have gained considerable ground. Here the elements and their connections are applied as pastes to the substrate by screen printing and subsequent firing. While the circuits so produced are sometimes bulkier than their thin film counterparts, they have the advantage of simpler and well-established manufacturing techniques, greater versatility in manufacture and fewer problems in making connections.

Silver and gold preparations capable of being screen printed have been available for many years for discrete component manufacture, and these are now employed in thick film integrated circuit production for connections and interconnections. Probably the most important new requirement for integrated circuits was a preparation capable of producing resistive films. This problem has been approached by developing suspensions, usually of powdered glaze (frit) and powders of one or more noble metals dispersed in an organic medium. After screening to the substrate, the preparation is fired to burn away the organic material, fuse the glaze component and complete any other reactions necessary. By varying the composition, a variety of different film resistivities can be produced but if close limits of resistance are required, they can be achieved by removal of part of the resistive film after firing.

Until recently the majority of the resistive preparations available required a temperature of 700°C or above, this high firing temperature being necessary to complete reactions within the preparation. This not only imposed the necessity of very close control of furnace atmosphere and of the firing cycle, but also limited the choice of substrate to materials such as high-alumina ceramics capable of withstanding this firing temperature. High surface finish of the substrate is necessary for this work, and mica and most glasses, which inherently have high surface finishes, were ruled out.

Against this background the Johnson Matthey Research Laboratories have developed glaze resistor preparations based on ruthenium dioxide. The objective was an ink incorporating a glaze based on a fully-reacted



One of the new Johnson Matthey preparations based on ruthenium oxide has been used in the production of these resistor plates by silk screening and firing. The substrate was mica, which required no surface treatment. One of the assembled but unencapsulated circuits is also shown in the photograph.

preparation that would be far less dependent on firing conditions than those hitherto available. To be viable the material had to satisfy three other conditions:

(1) The metal/glaze system had to be capable of producing a wide range of resistivities.
(2) The films had to have acceptably low temperature coefficients.
(3) The ruthenium had to be used as economically as possible.

Conduction through Ruthenium Dioxide

Ruthenium dioxide is a black, electrically conducting crystalline solid with the rutile structure. Unlike palladium oxide, it can be heated in air to 1100°C without physical or chemical change, and is almost completely insoluble in a wide variety of frit and glass compositions.

It can seldom, if ever, be prepared as stoichiometric RuO_2, and is usually partially defective in oxygen, with a corresponding amount of Ru^{3+} in place of Ru^{4+} in the crystal lattice. Valency control within narrow limits was obviously necessary if stable resistors based on ruthenium dioxide were to be developed.

Work on the control of deviating valencies in semiconducting oxides, in particular nickel oxide, was reported by E. J. W. Verwey and his co-workers at Philips in 1950 (1). It was shown that introduction of suitable ions into the lattice structure of a variable oxide could, without deforming it, balance the ions of deviating valency already within the lattice and still maintain overall neutrality. For example, Verwey obtained a composition $Li_{\delta}^{+}Ni^{2+}_{(1-2\delta)}\ Ni_{\delta}^{3+}O$ by calcining lithium carbonate with nickel oxide at 1200°C under oxidising conditions. The product had the same structure as nickel oxide, but with a smaller unit cell, and the Ni^{3+} content was broadly equivalent to the amount of lithium oxide added.

This suggested that valency variations in ruthenium dioxide might be controlled by a similar "doping" technique, leading to a better reproducibility from batch to batch, together with a measure of control over both resistivity and temperature coefficient.

Control of Valency

The oxides of Group Va metals were selected for investigation. Pentavalent ions would be necessary to balance the Ru^{3+} ions in the lattice and maintain overall neutrality, and M^{5+} ions of Group Va metals have a radius within ±15 per cent of that of the Ru^{4+} ion, which is about the limit for the entry of an ion of one species into the lattice of another in significant quantity. It was found that niobium pentoxide could be introduced into the ruthenium dioxide lattice in quantities up to 50 per cent molecular, and that the results obeyed Vegard's Law, which states in effect that the extent of the change in lattice parameter of the host oxide is proportional to the molecular percentage of added dopant. This linearity provides a useful means of monitoring the composition by X-ray diffraction before processing into a resistor preparation.

Moreover, since the temperature coefficient of resistance of ruthenium dioxide is metallic in nature and strongly positive, introduction of a non-conducting oxide might be expected to exert a negative influence on the temperature coefficient. Thus control of temperature coefficient in addition to resistivity might be achieved.

Further work showed that resistance values were largely governed by the ratio of doped ruthenium dioxide to glass, and temperature coefficients by this ratio in conjunction with the molecular percentage of niobium pentoxide in the ruthenium dioxide lattice. For example, ruthenium dioxide glaze films in a wide range of resistance values were found to have positive coefficients in excess of $1000 \times 10^{-6}/°C$. As the molecular percentage of niobium pentoxide in the calcine was increased the temperature coefficient decreased, reaching a negative value of $100 \times 10^{-6}/°C$ with 20 per cent molecular content of niobium pentoxide.

Since the niobium and ruthenium oxides are reacted by calcination before incorporation in the resistor preparation, no reaction occurs when the preparation is subsequently fired on the substrate, and electrical properties were not unduly affected by variations in the time of firing or in the temperature and atmosphere in the furnace.

Silver powder was found to be a useful addition to ruthenium dioxide based preparations. Up to 60 per cent of the ruthenium dioxide could be replaced with silver without adversely affecting the temperature coefficient provided a balance was struck between the niobium pentoxide and silver contents, the positive influence of the silver being compensated by the negative influence of the niobium pentoxide on the temperature coefficient. Thus silver provided an additional means of controlling temperature coefficient in addition to reducing the cost of the resistor preparation.

The Glaze Component

Investigation of the glaze component of the resistor compositions showed that this had a significant effect on some electrical properties. Glasses of the lead borosilicate type promoted high positive temperature coefficients, often exceeding $500 \times 10^{-6}/°C$ and $2000 \times 10^{-6}/°C$ respectively with doped and undoped ruthenium dioxide. Better results were obtained with zinc and cadmium borosilicate glasses.

Electrical Properties

At present four basic ruthenium oxide preparations are available commercially (2), covering the range from 100 to 3000 ohms/sq./mil., but it is expected that seven preparations will ultimately be produced, firing at 600°C upwards, to cover the range 5 to 100,000 ohms/sq./mil. Intermediate values may of course be obtained by blending the two standard compositions nearest to the desired resistance.

Little difficulty should be experienced in controlling values to within ±20 per cent of nominal, with the possibility of maintaining better than ±10 per cent with good machines under closely controlled conditions.

Temperature coefficients in the range -100 to $+100 \times 10^{-6}/°C$ can be expected with sheet resistivities from 50 to 1000 ohms/sq./mil. As resistivity increases the temperature coefficient tends to become more negative, and values of $+50$ to -250 can be expected with resistivities from 1000 to 10,000 ohms/sq./mil. For even higher resistivities temperature coefficients between -200 and -500 may be expected at present, but this may be reduced later to 0 to $-300 \times 10^{-6}/°C$.

Ruthenium dioxide glaze resistor films subjected to a load of $5W/in.^2/mil.$ at 70°C for 1000 hours showed a drift in resistance value of <0.5 per cent. Short duration power dissipation tests showed no drift in value at loadings of up to 100W/in^2/mil. The films showed good thermal stability with a drift of <0.5 per cent after ten cycles from +20° to 105°C, and a drift of <0.25 per cent after 2000 hours at 105°C without load.

Application to the Substrate

The organic medium in which the solid components are dispersed was formulated to give a paste with rheological properties suitable for screen printing. This process, with close control, allows deposition of even, well defined films ranging in thickness, when fired, from 0.002 to 0.0003 inch, largely depending on the design of the machine, the mesh size of the screen and the type of stencils used. Printing thickness was standardised at 0.0005 inch, using a 200 mesh stainless steel screen. This was considered suitable for all circuits except those in which unusually high power dissipation is necessary, when films up to 0.001 inch might be preferred.

The surface condition of the substrate was found to have an effect on the reproducibility of electrical properties of the fired films. The best results were obtained with smooth flat substrates such as mica, glass and high quality alumina ceramics, with centre line average values of smoothness below 5µ inch.

References

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Cobalt-Platinum Alloy Magnets

TEMPERATURE DEPENDENCE OF MAGNETIC PROPERTIES

Recent studies of cobalt-platinum alloys have shown the importance of crystal structure in relation to the exceptional magnetic properties which can be developed, particularly in the 50 atomic per cent alloy.

In work reported by Dr Hermann Dietrich of the Research Institute of Deutsche Edelstahlwerke, Krefeld, and reviewed in this journal (1), it was shown how the magnetic state of cobalt-platinum magnets was altered by heating to temperatures near the Curie point. More recently, the same author has reported the results of a further study of the temperature dependence of various cobalt-based permanent magnets, including cobalt-platinum, in which temperature coefficients of saturation magnetisation and demagnetisation curves were determined (2).

From the results of tests on small cylindrical cobalt-platinum magnets produced from melted and cast material, it was shown that variations in saturation magnetisation were small between −200°C and +200°C. Within this range the average saturation magnetisation was found to be 6750 gauss and this varied with temperature at the rate of −0.01 per cent per °C. A single Curie temperature was found at 530°C, despite the presence of a two-phase structure, indicating either that one phase only is ferro-magnetic or that the ordered and disordered phases have similar Curie temperatures.

Demagnetisation curves, shown as the relationship between intrinsic induction ($4\pi I$) and demagnetising field (H) at temperatures between −195° and 440°C, demonstrate the very high coercivity of the cobalt-platinum alloy. The 'rectangular' form of the curves in the lower temperature ranges indicates high stability under large demagnetising fields of at least 2000 oersteds, and while residual induction reduces more rapidly with increasing temperature, those magnets with a suitably high length : diameter ratio exhibit almost negligible temperature dependence between −195° and +200°C. Above 200°C the magnetic properties reduce rather more rapidly, but can still be restored by remagnetising until changes in structure, which start to occur at about 500°C, produce permanent changes in the demagnetisation curve.

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